Kinetic Study on the Thermal Decomposition of Copper(II) Oxalate

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The thermal decomposition of copper(II) oxalate has been studied under vacuum using a constant-volume apparatus and a microbalance; and under dynamic atmospheres of air, nitrogen and oxygen using thermogravimetry and differential scanning calorimetry. The decomposition was found to proceed to copper metal under an inert atmosphere and vacuum; while in air and oxygen, copper(II) oxide was found to be the decomposition product. In each case the decomposition was found to be exothermic with an enthalpy change of -9 ± 2 kJ mol⁻¹ in nitrogen and -134 ± 5 kJ mol⁻¹ in air. Isothermal kinetic analysis showed the data to fit an Avrami–Erofeev relationship with n = 3 in each case. Arrhenius parameters are reported for each decomposition atmosphere and are compared to those of other transition-metal oxalates which appear in the literature.

The presence of a preparation effect is noted, as seen with other oxysalts; however, no evidence for the formation of copper(I) oxalate has been found which has previously been speculated to be an intermediate in the decomposition.

The decomposition of copper oxalate has previously been studied¹ and is reported to take place in one stage from the anhydrous oxalate to the metal in an inert atmosphere.

$$CuC_2O_4 \rightarrow Cu + 2CO_2$$

The reaction was reported to be exothermic and the solid residue was activated to produce a solid with a surface area of $12 \text{ m}^2 \text{ g}^{-1}$; however, sintering of the product was rapid beyond 200 °C.²

Thermogravimetric (TG) experiments showed the production of copper in a nitrogen atmosphere but the oxide, CuO, in air,³ due to oxidation of the copper metal.

$$\operatorname{CuC}_2\operatorname{O}_4 \rightarrow [\operatorname{Cu}] \xrightarrow{1/2\operatorname{O}_2} \operatorname{CuO}$$

In the present study kinetic features of the decomposition are reported. An extended abstract regarding the studies on the decomposition in a vacuum has previously been presented.⁴ Here the results are given in more detail, and supplemented by kinetic data using thermogravimetry.

Copper oxalate is commonly quoted as having water of crystallization with the formula $CuC_2O_4 \cdot 1/2H_2O$. In the work reported here the anhydrous material was used, which could be prepared by heating at 120 °C. The environmental effect on the decomposition was noted by carrying out the thermal analysis in various atmospheres.

Experimental

The copper oxalate was prepared by combining 0.1 mol dm^{-3} aqueous solutions of copper nitrate and oxalic acid in the correct stoichiometric proportions. The non-stoichiometric preparations used in the investigation into the effect of sample preparation used a 2:1 copper nitrate to oxalic acid ratio for the excess copper nitrate preparation; and a 1:2 ratio for the excess oxalic acid preparation.

Constant-volume unit

Isothermal decomposition studies were carried out using a constant volume unit, previously described,⁴ in which the sample was decomposed under vacuum and the progress of decomposition noted by measuring the pressure of evolved

gas against time. In each experiment 3 mg of anhydrous copper oxalate was used.

Vacuum Microbalance Experiments

A vacuum microbalance assembly was also used for determining the kinetics of decomposition. In these experiments a sample size of 0.12 g was used.

Thermal Analysis

A DuPont 1090 work station was used, controlling a 951 TG unit and a 910 DSC.

For the thermogravimetry a platinum sample boat was used with the sample size being in the range 4–10 mg. The atmosphere flow rate was $30 \text{ cm}^3 \text{ min}^{-1}$.

For the DSC aluminium sample pans were used with the sample size in the range 10–17 mg. The heating rate was 5 K min⁻¹ and the atmosphere flow rate was 30 cm³ min⁻¹.

Adsorption Experiments

A low-temperature krypton adsorption unit was used to measure the surface area of the solid residue from thermal decomposition by a B.E.T. analysis. The details of this equipment and its use have previously been given.⁵

Results and Discussion

Experiments conducted under Vacuum Conditions

A series of isothermal decompositions were obtained using the constant-volume apparatus and the vacuum microbalance. The anhydrous copper oxalate was prepared by degassing under vacuum at 150 °C. The single-stage decomposition showed no initial surface reaction, and short induction and acceleratory periods.

The results from the constant-volume apparatus are shown in Fig. 1. A set of curves was also obtained after similar pretreatment using the vacuum balance and these are shown in Fig. 2.

Generally the analysis of the kinetic data showed either a Prout and Tompkins relationship or an Avrami-Erofeev relationship, with the latter giving the best fit. The pre-





Fig. 1 Isothermal decomposition curves for copper oxalate using constant volume apparatus. T/K: (a) 545.4, (b) 533.4, (c) 529.1, (d) 522.1, (e) 520.9

exponential term was altered by the experimental conditions, but the activation energy was around 125 kJ mol^{-1} .

The results from the constant-volume unit are best described by the Erofeev equation:⁶

$$-\log(1-\alpha) = kt^n$$

Over the range α (fraction decomposed) = 0.2-0.95 with n = 3 (see Fig. 3). In the above equation, and other kinetic equa-



Fig. 2 Isothermal decomposition curves for copper oxalate using automatic vacuum balance. T/K: (a) 533.4, (b) 522.2, (c) 514.4, (d) 508.9, (e) 505.6, (f) 503.6



Fig. 3 Avrami-Erofeev equation plot, $\ln[-\ln(1-\alpha)]$ vs. ln t, for copper oxalate decomposition data from constant volume unit at 545.4 K. n = 3.0

tions used here t = time of heating, and k is the temperaturedependent rate constant. However the Mampel contracting-sphere equation,⁷

$$1 - (1 - \alpha)^{1/3} = kt$$

also gave a reasonable fit over the range $\alpha = 0.675 - 0.925$.

The point of maximum rate is at $\alpha = 0.3$. The initial acceleratory period obeys a power law with n = 2.9 and the final stage of the reaction, *i.e.* from $\alpha = 0.80$ gives a reasonable fit with the first-order decay law. The activation energy for the overall reaction, calculated from the Ahrenius plot was found to be 136 kJ mol⁻¹.

The vacuum balance isothermal runs show a more marked acceleratory period, the maximum rate occurring at $\alpha = 0.50$, the curve being a fairly symmetric sigmoid shape, and the Prout–Tompkins equation⁸

$$\log\frac{\alpha}{1-\alpha} = kt$$

was found to fit the data fairly well but with different slopes over the range $\alpha = 0.1-0.5$ and $\alpha = 0.5-0.925$. However, the Erofeev equation gives a better fit, as shown in Fig. 4, again with different slopes over the ranges $\alpha = 0.05-0.50$ (n = 2.90) and $\alpha = 0.51-0.95$ (n = 3.57). Above $\alpha = 0.5$ the Mampel contracting-sphere relationship also seems to be obeyed. The kinetics of the acceleratory period can be described by a power law up to $\alpha = 0.5$ with n = 2.4 and the overall activation energy calculated from the Arrhenius plot was 128 kJ mol⁻¹, which agrees fairly well with the value obtained from the experiments on the constant-volume apparatus.



Fig. 4 Avrami-Erofeev equation plot, $\ln[-\ln(1-\alpha)]$ vs. $\ln t$, for copper oxalate decomposition data from vacuum microbalance at 533.4 K. (a) n = 3.57, (b) n = 2.90

The surface area of the initial oxalate was found to be 2.1 $m^2 g^{-1}$. However, on degassing at 150 °C for 19 h this increased to 8.9 $m^2 g^{-1}$.

The kinetics of decomposition of copper oxalate in a vacuum are therefore best described in terms of the Erofeev equation with n = 3. This implies rapid formation of nuclei which then undergo three-dimensional growth at a constant rate, forming compact nuclei. The initial acceleratory period described by the power law with n = 2.9 can be interpreted in terms of (a) instantaneous nucleation followed by the three-dimensional growth of compact nuclei or (b) the formation of nuclei at a linear rate with two-dimensional surface growth.

The former interpretation seems more probable in view of the applicability of the Erofeev equation throughout the reaction. Towards the end of the reaction a contracting interface would be set up, which would enclose isolated blocks of reactant.⁹ As the interface breaks down it is possible that some of these blocks would have no nuclei present, but more likely they would have patches of nucleated surface. This could explain why rather imperfect fits to the equations of Erofeev, Mampel and the unimolecular decay law are obtained since the process of growth and decay would be proceeding simultaneously in different parts of the decomposing material.

When the kinetics of decomposition are considered for the material decomposed on the vacuum balance using greater quantities of material, little difference from the above results are obtained.

The maximum rates were higher when the decomposition was carried out on the vacuum balance. This could be due to greater self-heating of the sample which decomposes exothermically, or it could be due to the effect of the accumulated 163

pressure of CO_2 above the material decomposing in the constant-volume apparatus. However, as this never exceeds 0.5 mmHg this is unlikely.

The kinetics of decomposition of copper oxalate in vacuum would appear to be similar to that already reported for nickel oxalate.¹⁰ The reaction kinetics for the decomposition in vacuum of cobalt oxalate differs from the data for copper and nickel in that the reaction obeys an exponential law.¹¹

The work on cobalt, nickel, copper and silver from these studies and those of others are reported in Table 1. The general trend for oxalates of copper and nickel is decomposition by an Erofeev relationship with n = 3, the early stages as expected obeying a cubic law (the form of the Erofeev equation reduces to a power law for small values of n). The indications here are that rapid nucleation precedes the growth of spherical nuclei,⁹ or that the nuclei form at a linear rate at the edges or surface cracks and then grow into cylindrical bodies.⁶

In this connection it is interesting to note that Dominey *et* $al.^{12}$ did suggest that cylindrical nuclei are formed during the low-temperature decomposition of nickel oxalate, although their interpretation of the parabolic law would not coincide with that of Erofeev. The latter investigator would suggest the formation of flat nuclei in this case (n = 2). The value n = 2 for the Erofeev equation obtained by Jacobs and Kureisky¹³ is at variance with the results of the present study and the work of Dominey *et al.*¹²

The explanation of the different results may be found in the method of preparation of the original oxalate. MacDonald and Hinshelwood,¹⁵ for example, showed that silver oxalate gave different results when prepared with an excess of silver nitrate and an excess of oxalic acid. Allen and Scaife¹⁶ found a similar effect with nickel oxalate. It is therefore probable that unless the method of preparation is identical in all cases and the original starting materials are all of the same purity the final decomposition kinetic expression could be different.

Another point that should be noted is that in the case of copper oxalate the decomposition data is fitted by the Erofeev equation and the Mampel equation and both these equations represent entirely different kinetic mechanisms. This emphasizes the difficulty of analysing the experimental curves and fitting the data to a model over restricted α ranges.

Effect of the Environmental Atmosphere on the Decomposition

From the respective weight losses and powder diffraction on the decomposition residue, the decomposition was confirmed to proceed to copper metal in inert atmospheres and copper(II) oxide in air.

In both atmospheres DSC showed a smooth 'bell'-shaped exothermic peak which on integration showed an enthalpy change of -9 ± 2 kJ mol⁻¹ in nitrogen, and -134 ± 5 kJ mol⁻¹ in air. These results can be compared to the -146 kJ mol⁻¹ obtained for the oxidation of copper metal to copper(11) oxide.

Isothermal decomposition curves were obtained for copper oxalate under atmospheres of nitrogen, air and pure oxygen, using the TG balance. These curves were treated by the conventional reduced time and α_{exp} vs. α_{theor} methods to obtain the reaction mechanism. The specific reaction rate constants were then calculated using the integral method.

$g(\alpha) = kt$

Results are shown in Table 2. As in the vacuum experiments, the Erofeev equation with n = 3 also holds for the experiments in dynamic atmospheres. However, under an atmosphere of nitrogen the expression holds only to $\alpha = 0.7$.

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Table 1 Summary of kinetics of decomposition of copper, nickel, cobalt and silver oxalate by gas-evolution techniques and vacuum microbalance techniques

	kinetic expression			$E_{\rm a}/{\rm kJ}~{\rm mol}^{-1}$			daaammaaitian
1	initial 2	main 3	range of α 4	initial reaction 5	induction period 6	main reaction 7	temperature range, T/°C 8
cobalt oxalate dehydrate at $150 ^{\circ}\text{C}$ (surface area $35 \text{m}^2 \text{g}^{-1}$) ref. 11	$\alpha_0 = 0.025$	E1 F0	0.05–0.50 0.40–0.95		204		298-315
dehydrated at 200 °C (surface area 16 m ² g ⁻¹) ref. 11	$\alpha_0 = 0.02$	B1 P3	0.02–0.98 0.75–0.95	163	225	165	305-320
silver oxalate ref. 14 ref. 6	not observed not observed	P4 A4			96	75	110–113
copper oxalate this study (constant-volume unit)	not observed	A3 P3 R3 F1	0.22-0.95 0.05-0.40 0.67-0.93 0.08-0.95	 	 	136	247–272
this study (vacuum balance)	not observed	A2.9 A3.57 P2.4 R3	0.05-0.50 0.50-0.95 0.07-0.5 0.50-0.98			127	235–261
nickel oxalate ref. 10	$\alpha_0 = 0.015$	E3.5 P3.3 F1	0.020.70 0.050.40 0.750.98				285 and 289 only
ref. 12 ref. 13	$ \begin{array}{l} \mathbf{R2} \\ \alpha_0 = 0.01 \\ \mathbf{R2} \end{array} $	A2 F1 acceleratory period only	0.05–0.84 0.56–0.97	138 138 159	216	138 151	240–280 230–260
	$\begin{array}{l} \alpha_{0}=0.02\\ (\text{low temp.})\\ \alpha=0.01\\ (\text{high temp.}) \end{array}$	P2 (low temp.) P3 (high temp.)					

χ ₀ ,	extent	of	initial	read	ction
des	ignatio	n o	f kinet	ic la	ws:

symbol	$g(\alpha) = kt$
Pn	α ^{l/n}
E1	ln α
An	$[-\ln(1-\alpha)]^{1/n}$
B 1	$\ln \left(\alpha / 1 - \alpha \right)$
R2	$1 - (1 - \alpha)^{1/n}$
R3	$1 - (1 - \alpha)^{1/3}$
F0	α
F1	$-\ln(1-\alpha)$

Above this temperature the decomposition is highly deceleratory and no kinetic expression could be found to describe its path.

The difference in the Arrhenius parameters may be explained by considering the reactions occurring. In nitrogen

Table 2 Arrhenius parameters from TG isothermal data

atmosphere	$E_{\rm a}/{\rm kJ}~{\rm mol}^{-1}$	A/s^{-1}	mechanism
nitrogen	154	1.22×10^{11}	A3
air	195	5.15×10^{14}	A3
oxygen	148	1.42×10^{10}	A3

atmospheres copper metal is produced as the decomposition product; however, in air the copper is reoxidized to copper(Π) oxide.

Figure 5 shows the oxidation of the copper metal to be a two-stage process, proceeding *via* copper(I) oxide. Hence as the copper nuclei are formed, in an atmosphere of air they are immediately oxidized. If the oxidation is considered to be the rate-determining step, in effect, the nuclei are poisoned and hence the activation energy is raised.

The retarding influence of oxygen has also been noted during the decomposition of silver oxalate.^{15,17} However, the decomposition proceeds to silver metal and no evidence for the formation of silver oxide has been found.



Fig. 5 Oxidation of copper metal in an atmosphere of air at a heating rate of 5 K min⁻¹.

Under an atmosphere of pure oxygen the rate of oxidation of the metal would be much greater and hence the decomposition would not be expected to be retarded to such an extent as under air. The activation energy in oxygen, however, is lower than that obtained in nitrogen. This may be explained to some extent in terms of self-heating of the sample due to the exothermic oxidation process.

The effect of sample preparation showed that preparation from non-stoichiometric quantitites of copper nitrate and oxalic acid both reduced the stability of the copper oxalate and caused the decomposition to occur by a more acceleratory process. This is in contrast to the results found for silver oxalate, in which the presence of excess silver nitrate stabilizes the salt, while the presence of excess oxalic acid reduces the stability. No attempts were made to study the kinetic aspects of these various preparations of copper oxalate.

The overall mechanism for decomposition of copper oxalate would seem to be similar to that already recorded for nickel oxalate.¹³ This involves the transfer of electrons from an oxalate ion to a metal ion:

$$C_2 O_4^{2^-} \rightarrow 2CO_2$$
$$A^{2^+} + 2e^- \rightarrow M$$

Ν

The ease with which this process occurs will partly depend on the electron affinity of the oxalate ion and the second ionization potential of the metal atom. Since the former is common to all cases considered, a qualitative correlation between the second ionization potential, the activation energy of the process, and the temperature of the decomposition might be expected. This is shown in Table 3. It can be seen that silver oxalate does not conform. It seems in this case that the overriding feature is the structure of the salt; the silver being

 Table 3 Dependence of temperature of decomposition and activation energy of ionisation potential

oxalate	2nd ionisation potential /eV	$E_{\rm a}/{\rm kJ}~{\rm mol}^{-1}$	decomposition temperature /°C
CO ²⁺	17.3	165	375
Ni ²⁺	18.2	138	355
Cu ²⁺	20.3	128	280
Ag ⁺	7.57 (1st)	75	140

monovalent with two atoms for every oxalate ion, thus making a closed ring structure impossible.

It is possible that during this redox step the sample preparation intrudes upon the decomposition. In the case of silver oxalate, MacDonald¹⁸ identified adsorbed nitrate ions as being the cause for the increased stability. If the first stage of the decomposition is considered to be dissociation into the various ions, then it would seem possible that the metal cation may react with the adsorbed ions on the surface, rather than be reduced by the oxalate anion and the decomposition would therefore be retarded. Although this theory adequately accounts for the trend shown by silver oxalate, it cannot explain the decrease in stability of copper oxalate when prepared with excess copper nitrate or oxalic acid.

It has been previously suggested¹⁹ that the thermal decomposition of various copper(II) carboxylates including copper oxalate proceed through the stepwise reduction of the cation. In our investigations we have found no evidence for the existence of copper(I) oxalate. In a powder diffraction study the orthorhombic structure was maintained until all trace of the copper(II) oxalate disappeared. The copper formed by the decomposition was found to exist in the form of face-centred cubic crystals, while the copper(II) oxide was in the form of face-centred monoclinic crystals.

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